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(54) **Antifreeze agents**

(57) An antifreeze agent comprises a water-soluble alcohol component, such as ethylene glycol, together with the following percentages by weight (all with reference to the alcohol component) of the following substances:

about 0.02 to about 1% alkali metal or ammonium metasilicate (calculated as pentahydrate), such as sodium metasilicate;

about 0.1 to about 5% alkali metal or ammonium salt of an aromatic substituted α,β -ethylenically

unsaturated carboxylic acid, such as sodium cinnamate;

about 0.5 to about 5% alkali metal or ammonium salt of boric acid, such as borax decahydrate;

0 to about 1% alkali metal or ammonium hydroxide, such as caustic soda;

0 to about 0.15% polycyclic heterocyclic copper corrosion inhibitor, such as benzotriazole;

0 to about 1% alkali metal or ammonium nitrite, such as sodium nitrite; and

0 to about 1% alkali metal or ammonium nitrate, such as sodium nitrate.

Certain of the chemical formulae appearing in the printed specification was submitted in formal form after the date of filing.

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SPECIFICATION
Antifreeze agents

This invention relates to antifreeze agents.

It is common practice to mix with the cooling water of an internal combustion engine an antifreeze

5 agent in order to depress the freezing point of the water and hence protect the engine against the
effects of cold weather. It is also known to add antifreeze agents to the circulating water of central
heating systems, particularly when the premises in which such systems are installed may be left vacant
in winter.

Such antifreeze agents conventionally comprise an alcoholic component, such as ethylene glycol,
10 diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, methanol or a mixture of two or
more of these. Since in time, acidic components may arise in the coolant, possibly due to oxidation of
the alcoholic component or, in the case of an engine, due to seepage of exhaust gases through a leak, it
is conventional practice to incorporate in an antifreeze agent one or more corrosion inhibitors in order to
protect the different metals with which the coolant may come into contact.

15 Engine blocks and cylinder heads, although formerly made almost exclusively from cast iron, may
alternatively be made from aluminium or an aluminium alloy. For the sake of convenience it is preferred
to formulate an antifreeze agent so that it is suitable for use both with cast iron and with aluminium
engine heads and/or blocks. Radiators are conventionally made from copper, copper alloy, or aluminium
20 alloy components soldered, glued or welded together. Other metallic parts with which an engine coolant
may come into contact include water pumps and thermostatic valves. An antifreeze agent is therefore
usually formulated with a view to providing, not only "reserve alkalinity" to provide a buffering effect
against acidic substances, but also corrosion protection to the metallic materials most commonly used
in engine manufacture, viz., iron, steel, cast aluminium, brass, solder and copper.

Amongst corrosion inhibitors that have previously been suggested there may be mentioned borax,
25 sodium mercaptobenzothiazole, sodium silicate, potassium or sodium phenylaminoacetate, alkaline
earth metal borates, triethanolamine, alkali metal and ammonium salts of phosphoric acid and of
polycondensed phosphoric acids, benzotriazole, alkali metal arsenites, alkali metal arsenates, alkali
metal molybdates, alkali metal tungstates, aliphatic, alicyclic or heterocyclic amines, sodium carbonate,
sodium nitrate, sodium nitrite, and sodium benzoate. Such inhibitors are conventionally used in a
30 combination of one to three, sometimes even more than three, compounds to prevent corrosion by
antifreeze agents, but they still do not act entirely satisfactorily. For example the presence of calcium
ions in the water may lead to precipitation of insoluble salts when the antifreeze agent contains
phosphate, arsenate, molybdate or tungstate ions; such insoluble calcium salts may lead to blockages in
the cooling system. Although polyphosphates can be added to solubilise calcium ions, they hydrolyse
35 and lose their activity. Amines attack copper and its alloys so sodium mercaptobenzothiazole may be
added to stop this. However, such antifreeze agents have unfavourable ageing characteristics and may
throw down precipitates on storage.

The specifications of three typical types of approved antifreeze agent are laid down in the
following British Standards: BS3150:1959, BS3151:1959 and BS3152:1959.

40 It is known to the expert in the art that weaknesses of individual inhibitors cannot be obviated
solely by accumulating corrosion inhibitors, but that it is often the case that good properties already
achieved are lost again upon the addition of further components. It is particularly difficult to develop an
inhibitor combination that will give good results under varying conditions and not only with a single test
and with only one kind of water. Moreover, although reserve alkalinity can be increased by increasing
45 the amounts of such inhibitors as borates or sodium carbonate, it is considered undesirable to
incorporate more than about 5% by weight of solids in the antifreeze agent lest undesirable quantities of
solids should build up in a cooling system on evaporation, for example by reason of engine overheating.
At least one vehicle manufacturer specifies today that, in order to qualify for approval for use in its
engines, an antifreeze agent must have a reserve alkalinity of at least 15 and a solids content of not
50 more than 5% by weight, based on the weight of the alcohol component.

According to the present Invention we provide an antifreeze agent comprising a water-soluble
alcohol component together with the following percentages by weight (all with reference to the alcohol
component) of the following substances:

about 0.02 to about 1% alkali metal or ammonium metasilicate (calculated as pentahydrate);
55 about 0.1 to about 5% alkali metal salt or ammonium salt of an aromatic substituted α,β -
ethylenically unsaturated carboxylic acid;
about 0.5 to about 5% alkali metal or ammonium salt of boric acid:
0 to about 1% alkali metal or ammonium hydroxide;
0 to about 0.15% polycyclic heterocyclic copper corrosion inhibitor;
60 0 to about 1% alkali metal or ammonium nitrite and
0 to about 1% alkali metal or ammonium nitrate.

Throughout this specification, except where otherwise specified, all percentages are by weight.

Preferably the alkali metal in the salts is sodium since sodium compounds are generally cheaper



than the corresponding compounds of other alkali metals. Other alkali metals that can be mentioned include lithium and potassium.

In addition to the listed essential and optional ingredients, the antifreeze agent may include one or more of the following further ingredients:

5. A minor amount (e.g. about 0.1% or less) of an amine or amino acid, e.g., phenylglycine; 5
 a minor amount of sodium benzoate;
 a minor amount of a dye, e.g., sodium fluorescein;
 a minor amount of antifoam agent.

The alcohol component may be any alcohol component conventionally used in antifreeze agents. It 10
 10 may be for example, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, methanol or a mixture of two or more thereof. It is preferred to avoid the use of methanol.

Typically the alcohol component is ethylene glycol.

Preferably the antifreeze agent contains from about 0.1 to about 0.3% alkali metal or ammonium metasilicate, based on the weight of the alcohol component, calculated as pentahydrate. The preferred 15
 15 metasilicate is sodium metasilicate. It is not necessary that the substance added to the antifreeze agent be a metasilicate; other forms of silicate can be utilised, provided that an appropriate quantity of alkali is added to adjust the Si:O ratio to 1:3. It is furthermore not necessary that sodium metasilicate be added as the pentahydrate; a corresponding amount of the anhydrous form or the nonahydrate or a mixture thereof or with the pentahydrate can be used instead.

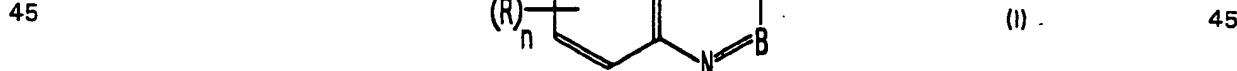
20 As aromatic substituted α,β -ethylenically unsaturated carboxylic acids, there can be mentioned, 20
 for example, acids containing one or more phenyl groups which can be substituted, for example by one or more alkyl (e.g., methyl or ethyl), nitro, or alkoxy (e.g., methoxy or ethoxy) groups. Typical such acids include cinnamic acid, β -naphthylacrylic acid, *p*-methoxycinnamic acid, *p*-methylcinnamic acid, *o*-nitrocinnamic acid, *m*-methoxy cinnamic acid, β -phenylcrotonic acid and the like.

25 The preferred aromatic substituted, α,β -ethylenically unsaturated carboxylic acid is cinnamic acid. 25
 This can be added to the antifreeze agent in the form of the free acid or preferably as one of its salts, e.g. the sodium, potassium, lithium or ammonium salt. Alternatively it can be incorporated in the antifreeze agent in the form of the corresponding aldehyde, i.e., cinnamaldehyde, since this compound will in time 30
 in use be oxidised to the corresponding acid. A preferred antifreeze agent thus contains about 0.1 to about 5%, for example about 0.3 to about 2%, based on the weight of the alcohol component, of sodium 30
 cinnamate.

35 The antifreeze agent of the invention contains a salt of boric acid, preferably a tetraborate, such as borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, or the corresponding lithium, potassium or ammonium salt, or a metaborate, such as sodium or potassium metaborate. The sodium salts will usually be preferred on the grounds of expense. The borax content may range from about 0.5 to about 5%, but preferably lies in the range of from about 1 to about 3%, based on the weight of the alcohol component. Mixtures of a tetraborate and a metaborate can alternatively be used. 35

40 An optional ingredient is an alkali metal or ammonium hydroxide, for example sodium hydroxide, or potassium hydroxide, in an amount of 0 to about 1%, preferably about 0.01 to about 0.05%, based on the weight of the alcohol component. By incorporating a small amount of an alkali metal or ammonium hydroxide in the antifreeze agent, it is possible to increase its reserve alkalinity without significantly 40
 increasing the solids content.

Another optional component is a polycyclic heterocyclic copper corrosion inhibitor. Among typical inhibitors of this kind there can be mentioned compounds of the general formula



in which R is selected from alkyl, alkoxy, and nitro, n is 0, 1, 2, 3 or 4, A represents $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, or $-\text{NR}'-$, R' represents optionally substituted alkyl, B represents $=\text{CH}-$, $=\text{C}(\text{SH})-$, $=\text{N}-$, $=\text{C}(\text{SM})-$, and M is an alkali metal. Examples of suitable compounds of formula (I) include benzotriazole, tolyltriazole, and mercaptobenzothiazole.

50 Other compounds of formula (I) include 2-mercaptobenzoxazole, 4-ethyl-2-mercaptobenzothiazole, 2-mercaptop-4, 5-dimethyl benzothiazole, 2-mercaptobenzimidazole, benzimidazole, benzotriazole, 4-methylbenzotriazole, 5-methylbenzothiazole, 4-methylbenzimidazole and 5,6-dimethylbenzimidazole, as well as the ammonium, sodium and potassium salts of the aforementioned mercapto compounds. If the antifreeze agent contains a compound of formula (I), e.g.,

benzotriazole, then it is preferably present in an amount of from about 0.05 to about 0.15% based on the weight of the alcohol component.

If a nitrite is added, e.g. sodium or potassium nitrite, it is preferred to utilise from about 0.05 to about 0.3% based on the weight of the alcohol component.

5 The preferred nitrates are sodium nitrate and potassium nitrate. 5

The antifreeze agent of the present invention can be prepared in any convenient manner, preferably by admixing with the alcohol component the specified additives in the amounts indicated. Preferably the antifreeze agent comprises at least about 85%, and usually at least about 95% up to about 99.38% of the alcohol component; it may further comprise a small amount, for example, less than 10 about 5% by weight, of water, based upon the weight of the alcohol component. Such small amounts of 10 water may assist in solubilising some of the additives.

As examples of suitable antifoam agents there may be mentioned silicone oils, polyglycols (e.g., polyoxypropylene glycols of molecular weight about 950 to 1950 which have been reacted with ethylene oxide to give copolymers containing up to about 30% by weight of ethylene oxide residues), 15 mineral oils, *iso*-octanol, C₈ to C₁₂ alcohols (e.g., C₇ to C₉ Oxo alcohols), organic phosphates, alkyl lactates and castor oil soaps. Such antifoam agents may be added, for example, in amounts of from about 0.0005 to about 0.05%, based on the weight of the alcohol component. 15

The amounts of boric acid salt and of alkali hydroxide or ammonium hydroxide are preferably so chosen that the pH of a 25 vol.% solution in distilled water of the antifreeze agent is not greater than 20 about 10.0 and preferably lies in the range of from about 7.5 to about 8.5. Moreover the agent is 20 preferably so formulated that its solids content is less than about 5% by weight, based on the weight of the alcohol component and its reserve alkalinity is at least about 15.

The antifreeze agents of the present invention are suitable for use as, for example, about 10 to about 60 vol.% aqueous solutions in the cooling systems of internal combustion engines. Usually they 25 will be utilised as about 20 to about 33 vol.% aqueous solutions for this purpose. They can also be used 25 in domestic and other circulating water central heating systems as well as in other equipment.

The invention is further illustrated in the following Examples. In these Examples the results were obtained using the glassware test apparatus described in BS 5117:1974 "Methods of Test for Corrosion Inhibition Performance of Antifreeze Solutions" published by British Standards Institution, 2 30 Park Street, London W1A 2BS. 30

EXAMPLE 1.

An antifreeze agent was prepared by admixing with 100 parts by weight of ethylene glycol (ethanediol) the following constituents:

	<u>Constituent</u>	<u>Parts by weight</u>	
35	Borax decahydrate	2.5	35
	Sodium nitrite	0.15	
	Benzotriazole	0.15	
	Cinnamic acid	1.32	
	Caustic Soda	0.40	
40	Disodium metasilicate pentahydrate	0.20	40

Upon testing in the glassware test (BS 5117:1974) the mean weight loss per specimen at 20 vol.%, 25 vol.%, and 33½ vol.% (diluted with standard test water) was as shown in Table 1. After testing, the specimens were chemically cleaned, prior to weighing, in order to remove adhered corrosion 45 products. 45

TABLE 1

	Copper	Solder	Brass	Mild steel	Cast iron	Cast aluminium
20 vol %	1.0mg	1.5mg	1.5mg	1.0mg	1.0mg	2.5mg
25 vol %	1.0mg	1.0mg	0.0mg	1.0mg	1.0mg	1.5mg
33½ vol %	2.0mg	0.5mg	0.0mg	2.0mg	1.5mg	2.5mg

The antifreeze agent of this Example has a solids content of 4.72% and showed a "reserve alkalinity" of over 15. For comparison an antifreeze composition of the type described in United Kingdom Specification No. 945638 was made up having a solids content of 4%; this had the following composition:

5

	<u>Constituent</u>	<u>Parts by weight</u>	
	Ethylene glycol	100	
	Borax decahydrate	1	
	Potassium nitrate	0.3	
10	Sodium nitrite	0.35	10
	Sodium benzoate	2.26	
	Sodium metasilicate	0.03	
	Benzotriazole	0.07	

The "reserve alkalinity" of this composition was 9.5. "Reserve alkalinity" is defined (according to 15 BS 5117:1974) as the number of millilitres of 0.1 N hydrochloric acid required for titration of 10 ml of concentrated antifreeze, or its equivalent, to a pH value of 5.5. Usually a 10 ml sample of antifreeze is diluted to 100 ml with distilled water prior to titration.

15

EXAMPLE 2.

Three antifreeze agents (hereafter called, A, B and C), were prepared each by adding to 100 parts 20 by weight of ethylene glycol the following ingredients:

20

	<u>Constituent</u>	<u>Parts by weight</u>	
	Borax decahydrate	2.5	
	Sodium nitrite	0.15	
	Benzotriazole	0.15	
25	Cinnamic acid	1.32	25
	Disodium metasilicate pentahydrate	0.1	
	Caustic soda	x*	

(*See Table 2 below)

30 These agents gave rise to the results listed in Table 2 upon testing according to the glassware test (BS 5117:1974) at 33½ vol.% (i.e. 33½ vols. agent mixed with 66½ vols. standard test water).

30



TABLE 2

Agent	x	Weight loss per specimen in mg.							pH
		Copper	Solder	Brass	Mild steel	Cast iron	Cast aluminium		
A	0.35	0	2	1	+2	1	2	7.8	
B	0.40	1	0	1	0	0	1	7.85	
C	0.50	1	2	0	+2	1	0	8.0	

All specimens were chemically cleaned to remove adherent corrosion products prior to weighing.
A plus sign (+) in front of a reading indicates a weight gain. Each of agents A to C had a "reserve alkalinity" of more than 15 despite having solids contents (based on ethylene glycol) of only 4.57%,

5 4.62% and 4.67% respectively.

5

EXAMPLE 3.

Two antifreeze agents (hereafter called D and E) were made by adding to 100 parts by weight of ethylene glycol the following ingredients:—

		Constituent	Parts by weight	
10		Borax decahydrate	2.5	10
		Sodium nitrite	0.15	
		Benzotriazole	0.15	
		Cinnamic Acid	1.32	
15		Disodium metasilicate pentahydrate	y**	15

(**See Table 3 below)

These 3 antifreeze agents were subjected to the glassware test of BS 5117:1974 and gave the results listed in Table 3 at 15 vol.% (i.e. 15 vols. of agent diluted with 85 vols. standard test water).

TABLE 3

Agent	y	Weight loss in mg per specimen						
		Copper	Solder	Brass	Mild steel	Cast iron	Cast aluminium	
D	0.32	0	2	1	+1	0	0	
E	0.20	1	2	2	0	2	13	

20 Both agents D and E had a "reserve alkalinity" of more than 15, despite a solids content (based on the weight of ethylene glycol) of only 4.44% and 4.32% respectively.

20

EXAMPLE 4.

An antifreeze agent is prepared according to the directions given in Example 1 except that the 0.15 parts by weight of benzotriazole is replaced by 0.15 parts by weight of tolyltriazole. Similarly good 25 results are obtained.

25



CLAIMS

1. An antifreeze agent comprising a water-soluble alcohol component together with the following percentages by weight (all with reference to the alcohol component) of the following substances:

about 0.02 to about 1% alkali metal or ammonium metasilicate (calculated as pentahydrate);
about 0.1 to about 5% alkali metal salt or ammonium salt of an aromatic substituted α,β -
ethylenically unsaturated carboxylic acid;
about 0.5 to about 5% alkali metal or ammonium salt of boric acid;
0 to about 1% alkali metal or ammonium hydroxide;
0 to about 0.15% polycyclic heterocyclic copper corrosion inhibitor;
0 to about 1% alkali metal or ammonium nitrite and
0 to about 1% alkali metal or ammonium nitrate.

2. An antifreeze agent according to claim 1, further including one or more of the following ingredients:

15 a minor amount of an amine or amino acid;
a minor amount of sodium benzoate;
a minor amount of a dye;
a minor amount of an antifoam agent.

15

3. An antifreeze agent according to claim 1 or claim 2, wherein the water-soluble alcohol component comprises ethylene glycol.

20 4. An antifreeze agent according to any one of claims 1 to 3, which contains from about 0.1 to 20
about 0.3% of sodium metasilicate, based on the weight of the alcohol component, calculated as pentahydrate.

5. An antifreeze agent according to any one of claims 1 to 4, wherein the aromatic α,β -ethylenically unsaturated carboxylic acid is cinnamic acid.

25 6. An antifreeze agent according to claim 5, which contains from about 0.3 to about 2%, based on 25
the weight of the alcohol component, of sodium cinnamate.

7. An antifreeze agent according to any one of claims 1 to 6, which contains from about 1 to about 3%, based on the weight of the alcohol component, of borax.

8. An antifreeze agent according to any one of claims 1 to 8, which contains from about 0.05 to
30 about 0.3%, based on the weight of the alcohol component, of sodium or potassium nitrite. 30

9. An antifreeze agent according to any one of claims 1 to 9, which contains from about 0.05 to about 0.15% based on the weight of the alcohol component, of benzotriazole.

10. An antifreeze agent according to any one of claims 1 to 9, which contains from about 0.01 to about 0.05%, based on the weight of the alcohol component, of sodium hydroxide or potassium hydroxide.

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